REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	**2. REPORT TYPE**	**3. DATES COVERED** *(From - To)*
July 2015	Briefing Charts	July 2015-August 2015

4. TITLE AND SUBTITLE
Synthesis and Reactivity of Backfluorinated NHC Carbene Complexes (Briefing Charts)

5a. CONTRACT NUMBER
In-House

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Rusty L. Blanski and Robert H. Grubbs

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER
Q1CC

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/RQRP
10 E. Saturn Blvd.
Edwards AFB, CA 93524-7680

8. PERFORMING ORGANIZATION REPORT NO.

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Air Force Research Laboratory (AFMC)
AFRL/RQR
5 Pollux Drive
Edwards AFB CA 93524-7048

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AFRL-RQ-ED-VG-2015-302

12. DISTRIBUTION / AVAILABILITY STATEMENT
Distribution A: Approved for Public Release; Distribution Unlimited.

13. SUPPLEMENTARY NOTES
Briefing Charts presented at American Chemical Society National Meeting; Boston, MA; 17 August 2015. PA#15448.

14. ABSTRACT
Briefing Charts

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			Wesley Hoffman
Unclassified	**Unclassified**	**Unclassified**	SAR	28	**19b. TELEPHONE NO** *(include area code)* 661-275-5768

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. 239.18

AFRL

THE AIR FORCE RESEARCH LABORATORY

LEAD | DISCOVER | DEVELOP | DELIVER

Synthesis and Reactivity of Backfluorinated NHC Carbene Complexes

Dr. Rusty Blanski

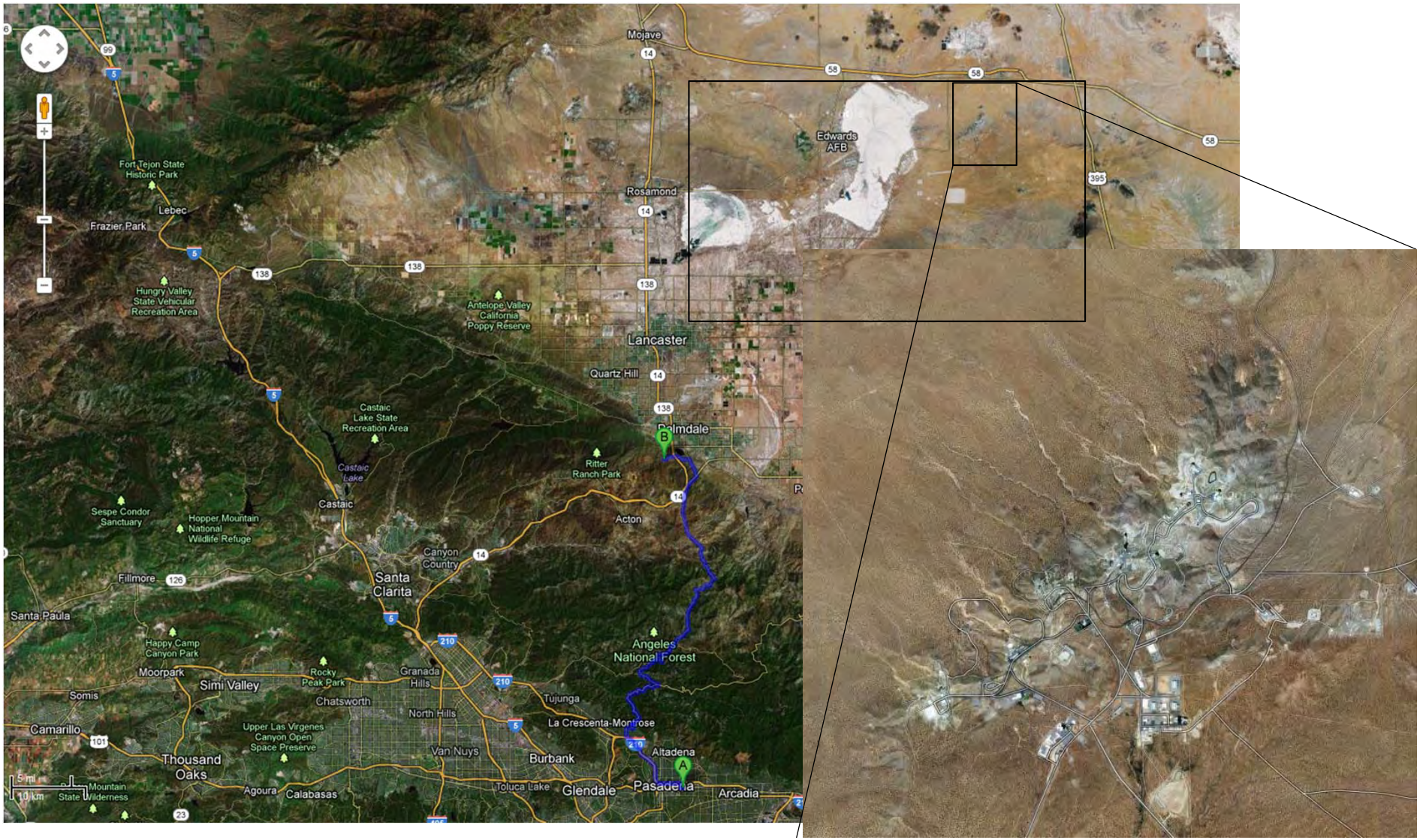
High Temp Components Group (RQRC)
Air Force Research Laboratory Edwards AFB, CA

Professor Robert H. Grubbs
California Institute of Technology,
Pasadena, California

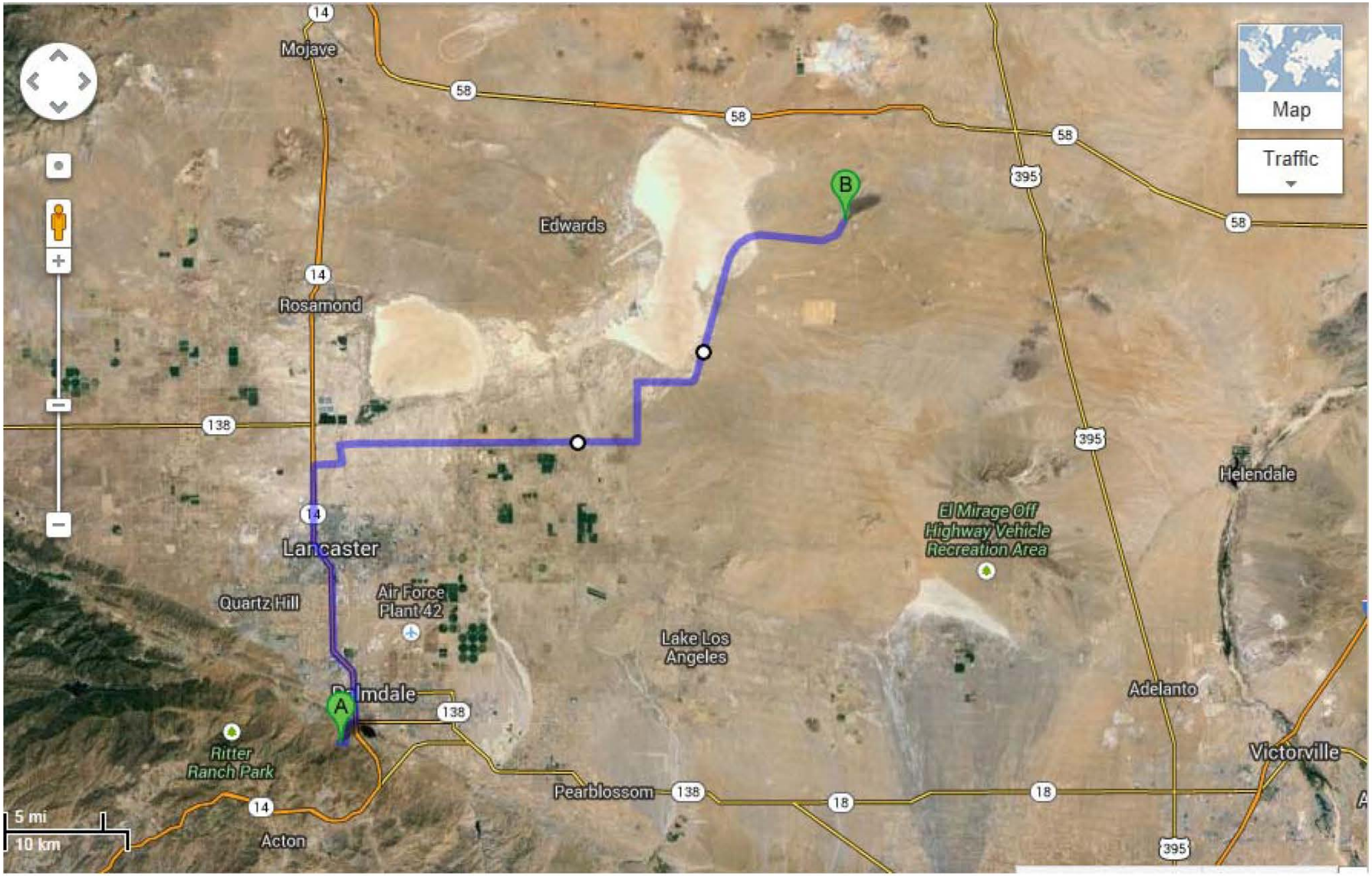
Introduction

- Introduction
- Proposed Research Overview
- Synthesis of Backfluorinated NHC Carbene Precursors
  - Synthesis of Ir complexes
  - IR study of Ir dicarbonyl complexes
  - Synthesis of Ru complexes
  - Reactivity of Ru complexes
- Conclusions and Future Directions

Edwards AFB – AFRL
Rocket Propulsion Research



Palmdale to AFRL: 53 miles
Located in the Middle of Nowhere

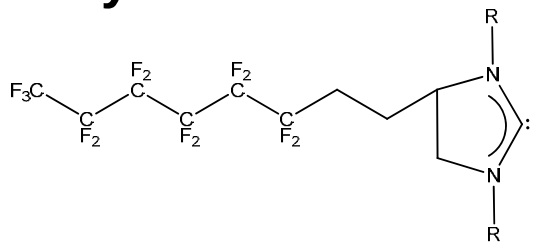


Edwards AFB

- **History**
  - Originally known as Muroc Army Air Corps Base
  - Test flights of the YB-42 (first American Jet) in the early ‘40s
  - Location where Chuck Yeager broke the Sound Barrier in the Bell X-1 (Original craft at the Smithsonian)
  - X-15 sub-orbital flights in the ‘60s (Armstrong)
- **AFRL**
  - Tenant of Edwards AFB since late ‘50s
  - Full scale testing of the Atlas rockets (Gemini missions)
  - Initial testing of the F-1 engine (Apollo missions) performed on site in the mid ‘60s
  - Large scale testing of solid rocket motors (Titan IV)
  - “Iranian nuclear facility” destroyed by the Transformers in “Transformers: The Dark side of the Moon”

Edwards AFB – AFRL
Projects

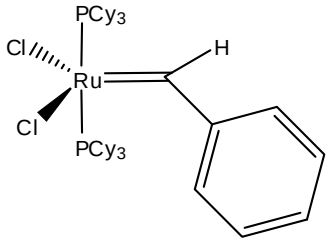
- **The Air Force has an interest in NHC carbene precursors for a variety applications**
  - **Ionic liquid propellants and additives**
  - **Ligands for Supercritical Chemical Fluid Deposition (SCFD)**
- **The Air Force also has an interest in fluorinated NHC carbenes**
  - **perfluoroalkyl chains generally known to improve solubility of systems in supercritical fluids**
  - **“Backfluorinated” NHC carbenes to improve solubility in supercritical fluids and perhaps maintain ligand stability**
  - **Surprisingly, the backfluorinated systems have never been reported**



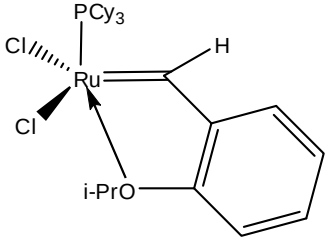
Potential for Collaboration
Backfluorinated NHC-Ru Catalysts

- **It was an easy leap to see that this technology should be applicable to other research areas**
  - **Hydrogenation in fluorinated solvents**
  - **Organic transformations in fluorinated solvents**
  - **Olefin metathesis in fluorinated solvents**
    - **Perhaps improved olefin metathesis of fluorinated olefins**
- **Questions**
  - **How does the addition of a perfluoroalkyl chain to the back of an imidazolinylidene ligand affect its electronic properties?**
  - **How does the addition of a perfluoroalkyl chain to the back of an imidazolinylidene ligand affect the catalytic properties of the ruthenium alkylidene complexes?**
  - **Does the addition of perfluoralkyl chains improve the solubility of Ru alkylidene complexes in fluorinated solvents?**

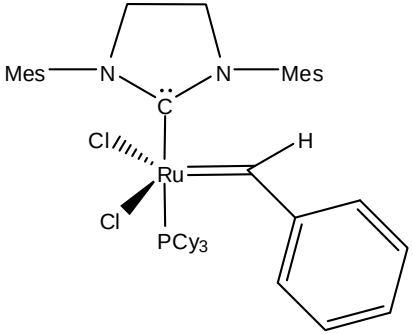
Fluoroalkene Metathesis



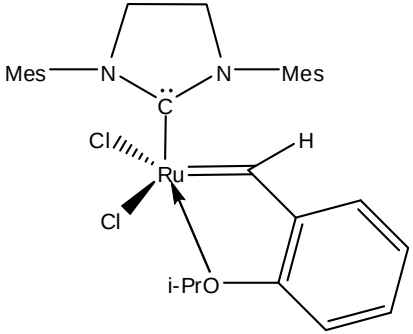
1st Generation Grubbs' Catalyst



1st Gen Grubbs-Hoveyda Catalyst



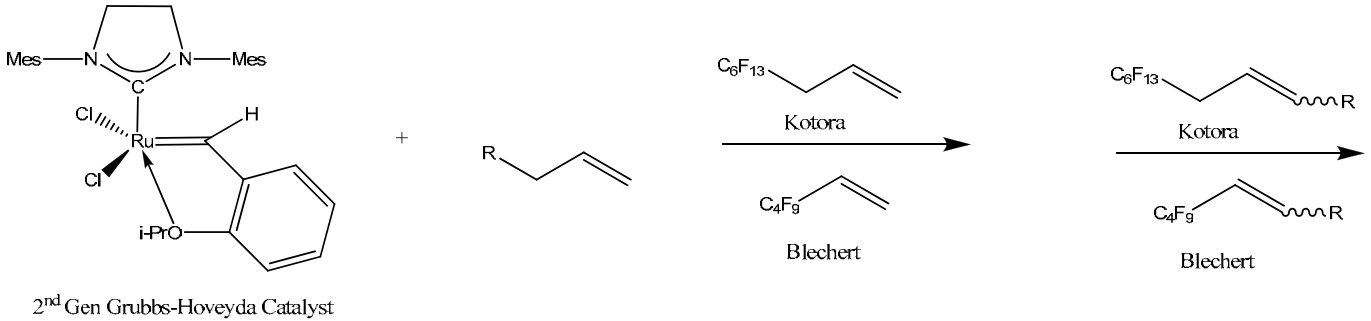
2nd Generation Grubbs' Catalyst



2nd Gen Grubbs-Hoveyda Catalyst

- **Fluoroalkene metathesis first reported by Blechert in 2001**
- **1st generation systems not effective**
- **2nd generation systems are effective**
  - **2nd Generation Grubbs-Hoveyda most effective**

Fluoroalkene Metathesis

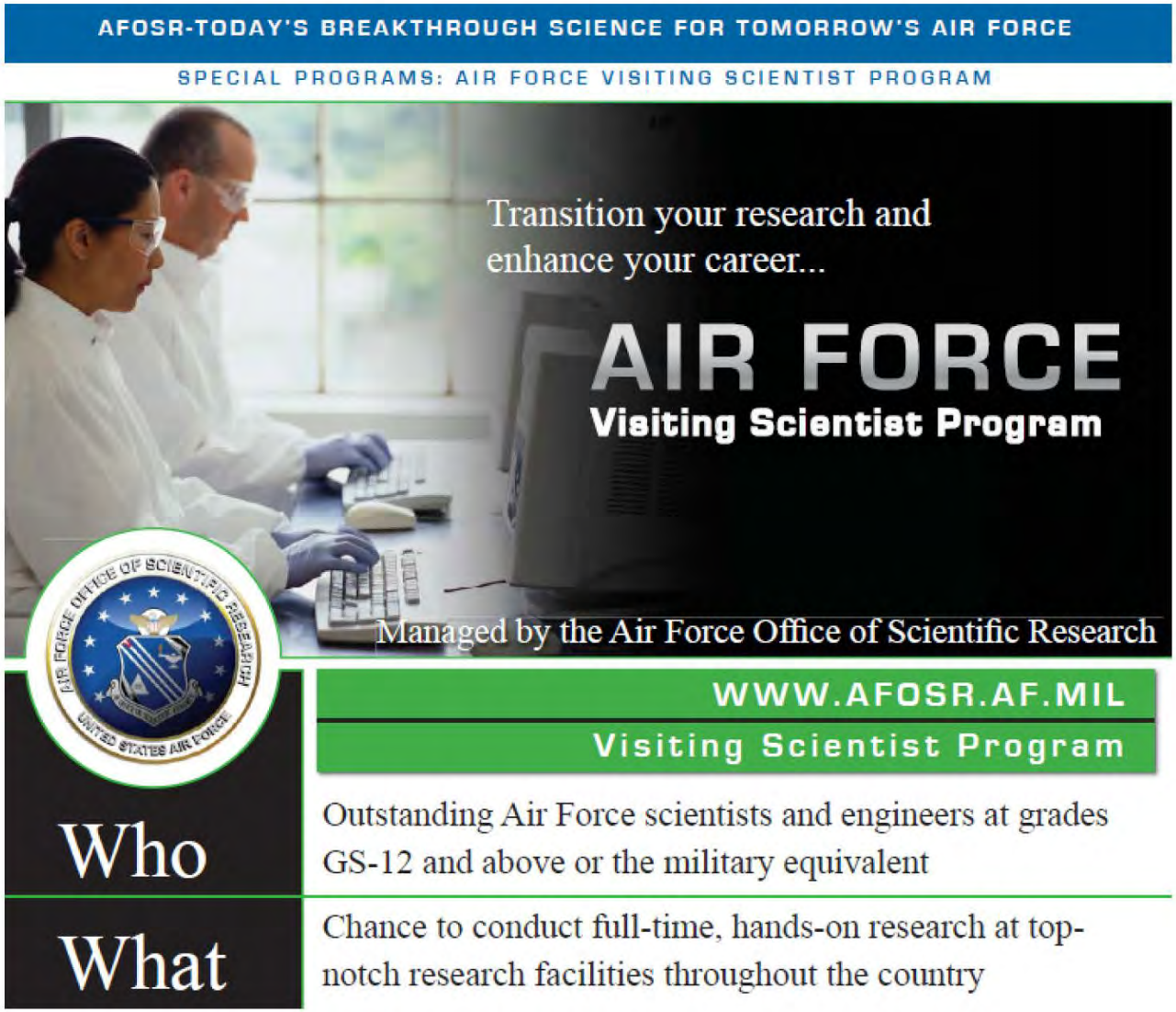


2nd Gen Grubbs-Hoveyda Catalyst

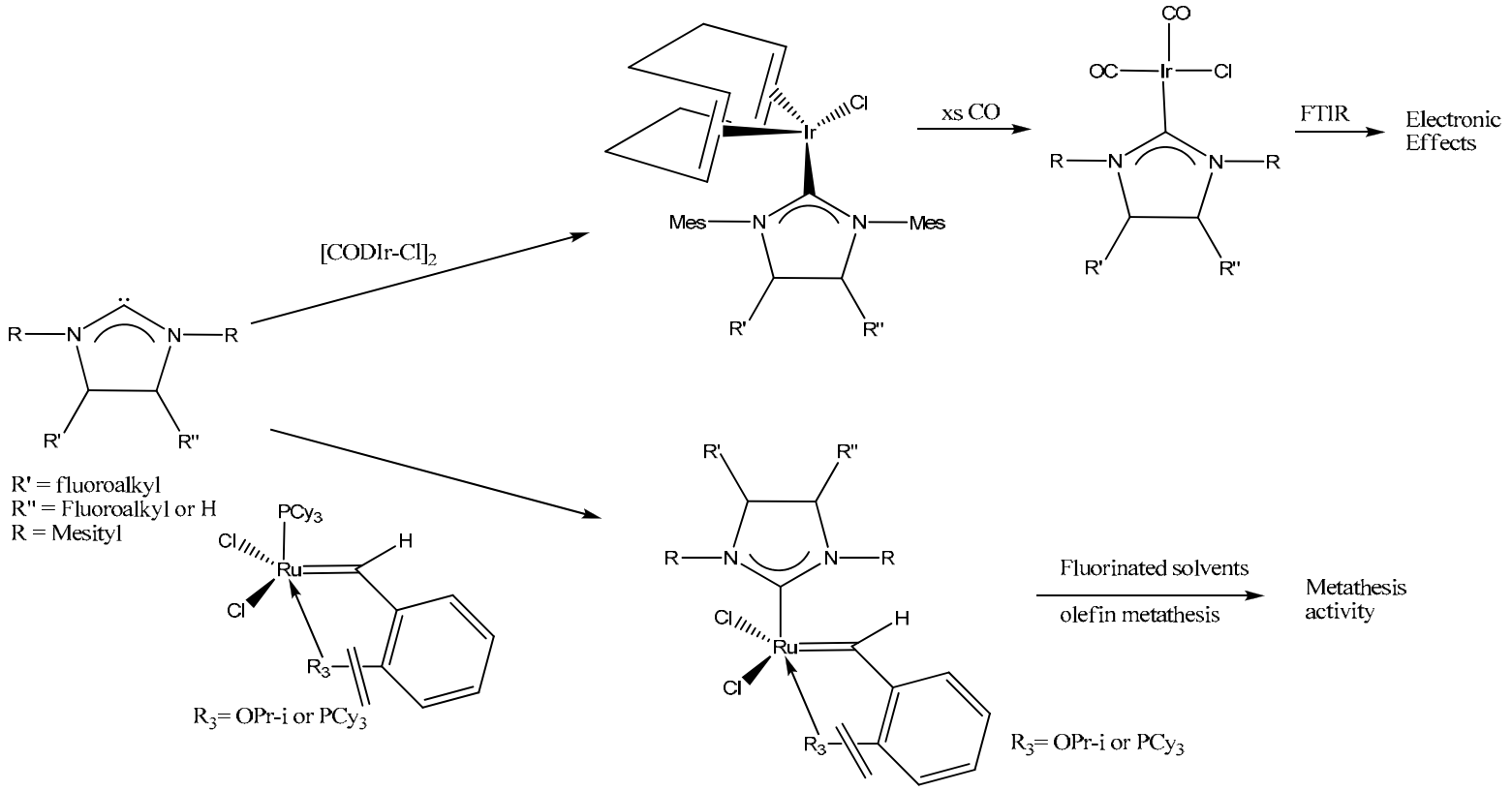
- **Blechert (2001) found that cross metathesis of perfluorobutyl(ethene) and various allylics required 10 mol% of catalyst with generally good yields (7-95+%)**
- **Kotora (2010) found that the cross metathesis of perfluorohexyl(propene) and various allylics was effective for several systems but the yields varied considerably (11-70% yield)**
- **Also, when the perfluoroalkyl chain is longer (perfluorooctyl-, perfluorodecyl-), personal research suggests that the catalyst has solubility issues**

AFOSR Visiting Scientist Program

6 Month Sabbatical to Research Institutions

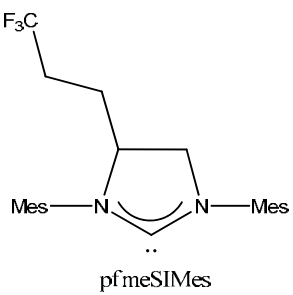


Proposed Research

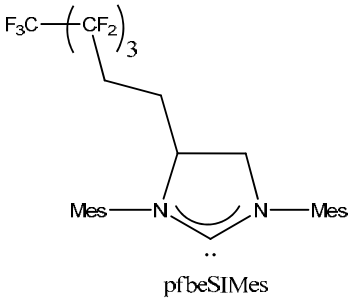


- **Electronic effects will be investigated**
  - **Effect of perfluoroalkyl length and methylene "buffer" length**
- **Olefin metathesis activity will also be investigated**

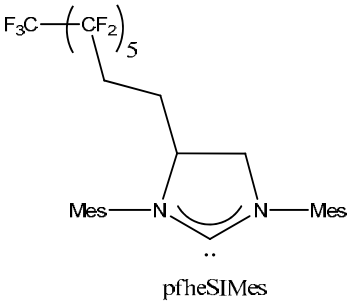
Synthetic Targets
Imidazolinidene Complexes



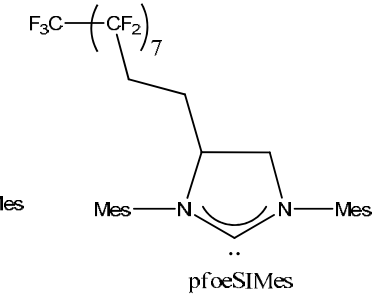
pfmeSIMes



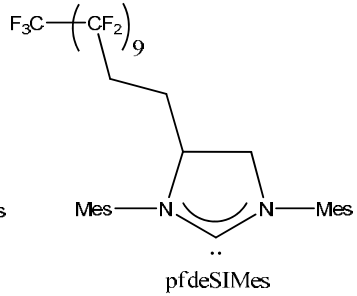
pfbeSIMes



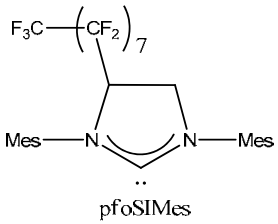
pfheSIMes



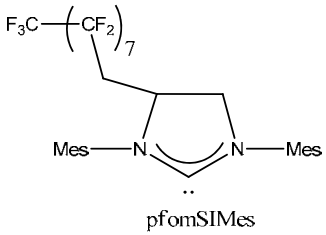
pfoeSIMes



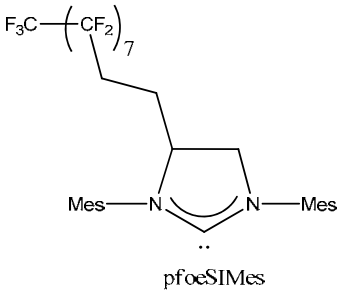
pfdeSIMes



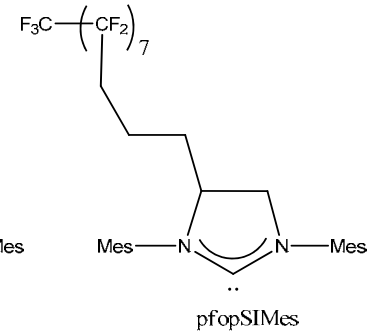
pfoSIMes



pfomSIMes



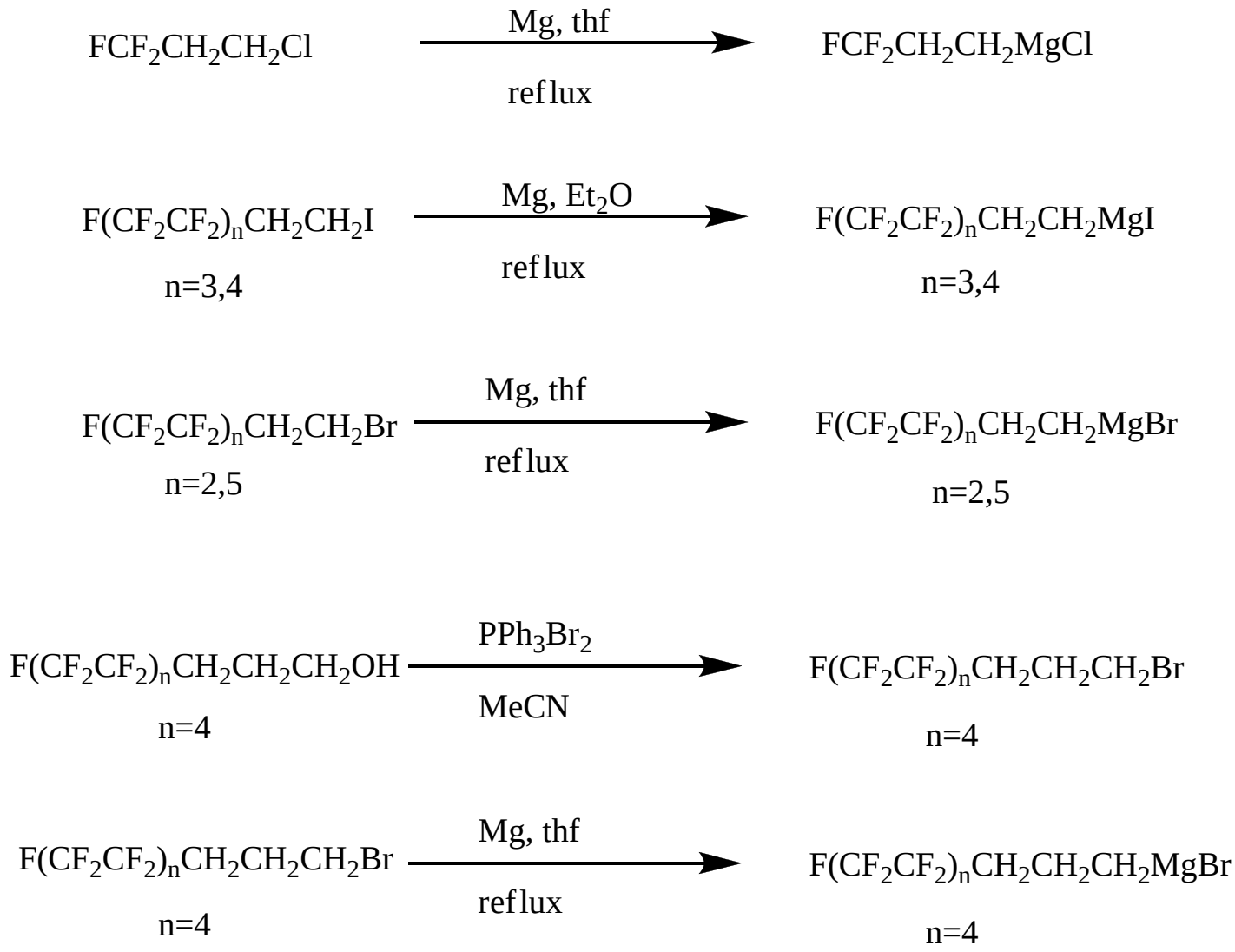
pfoeSIMes



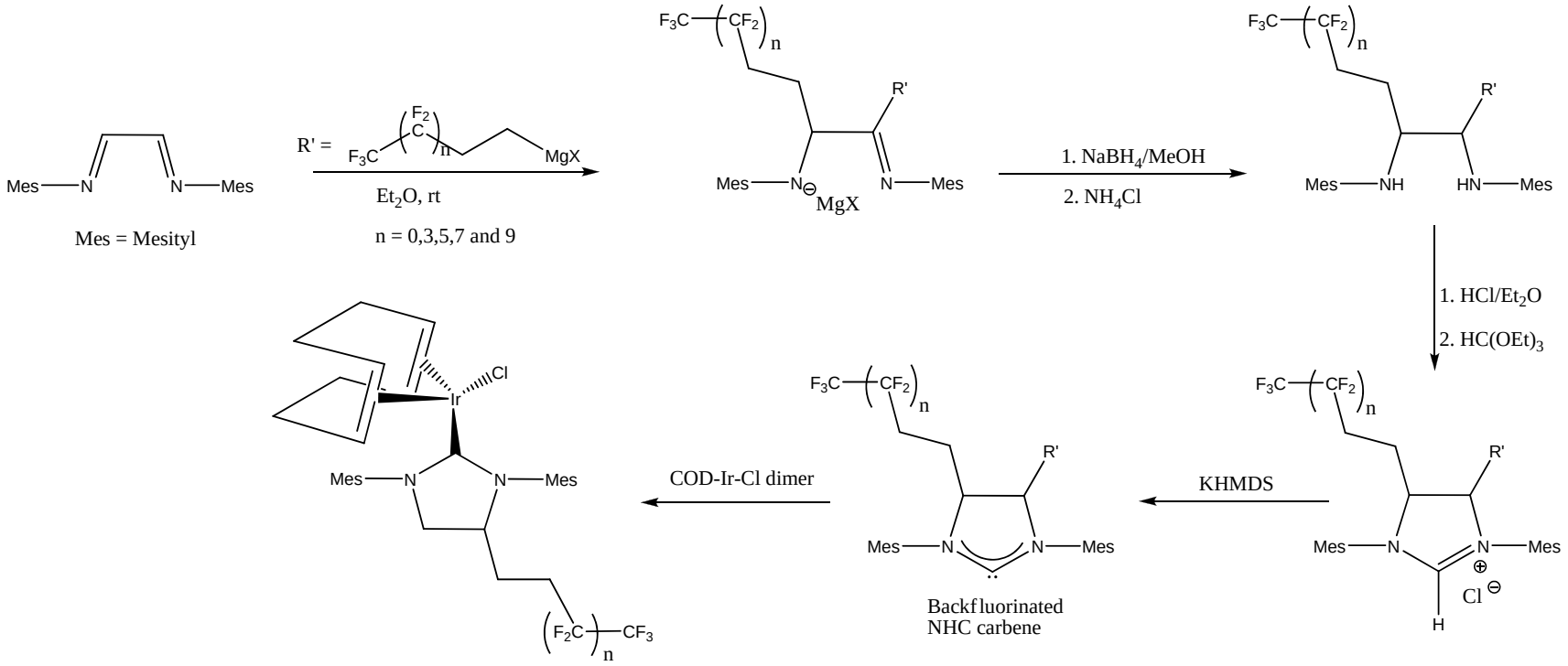
pfopSIMes

- **Perfluoroalkyl chain length and “Buffer” length will be investigated**

Preparation of Perfluoroalkyl Grignard Reagents

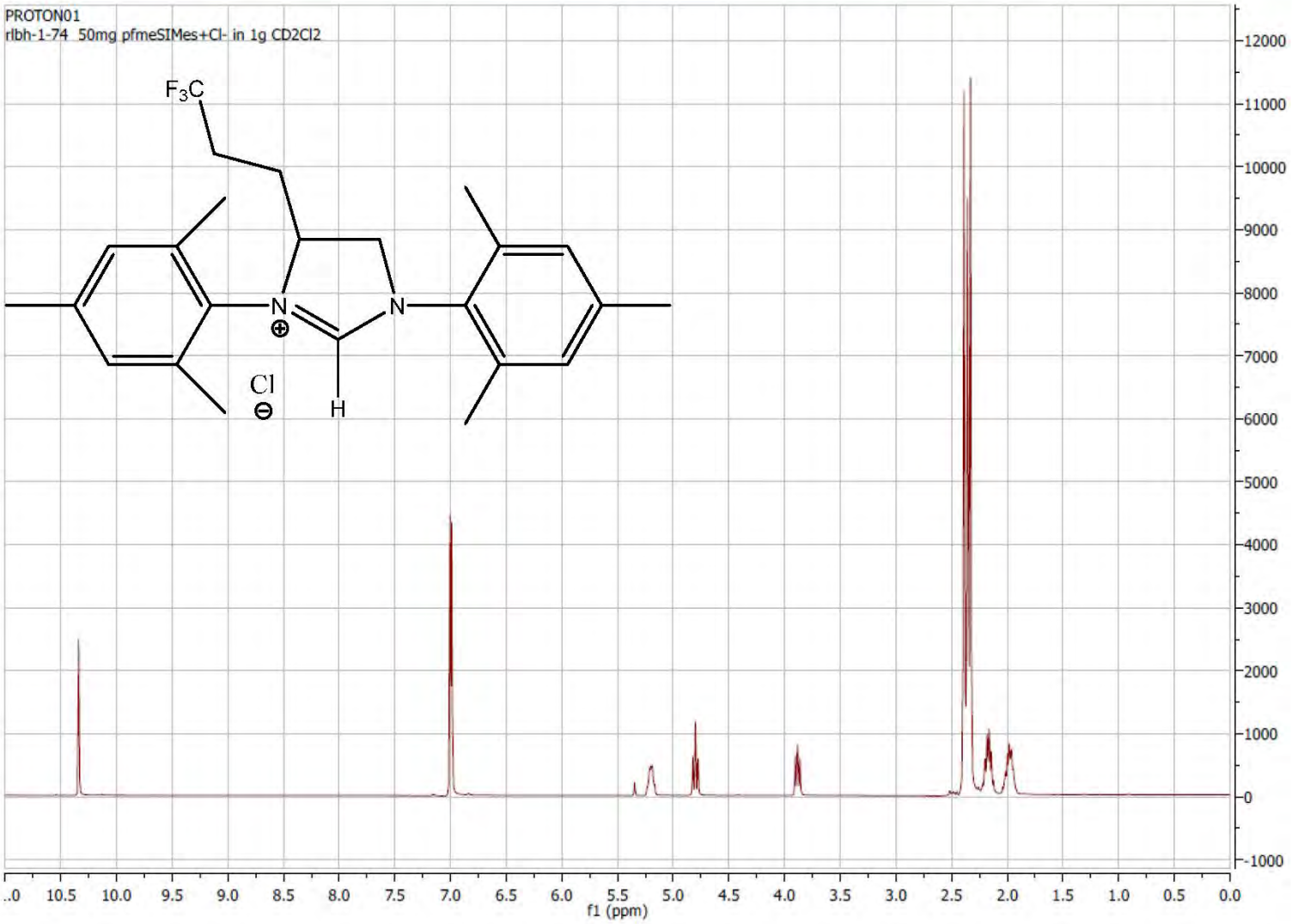


Synthetic Method #1
Grignard Addition/Reduction/Cyclization

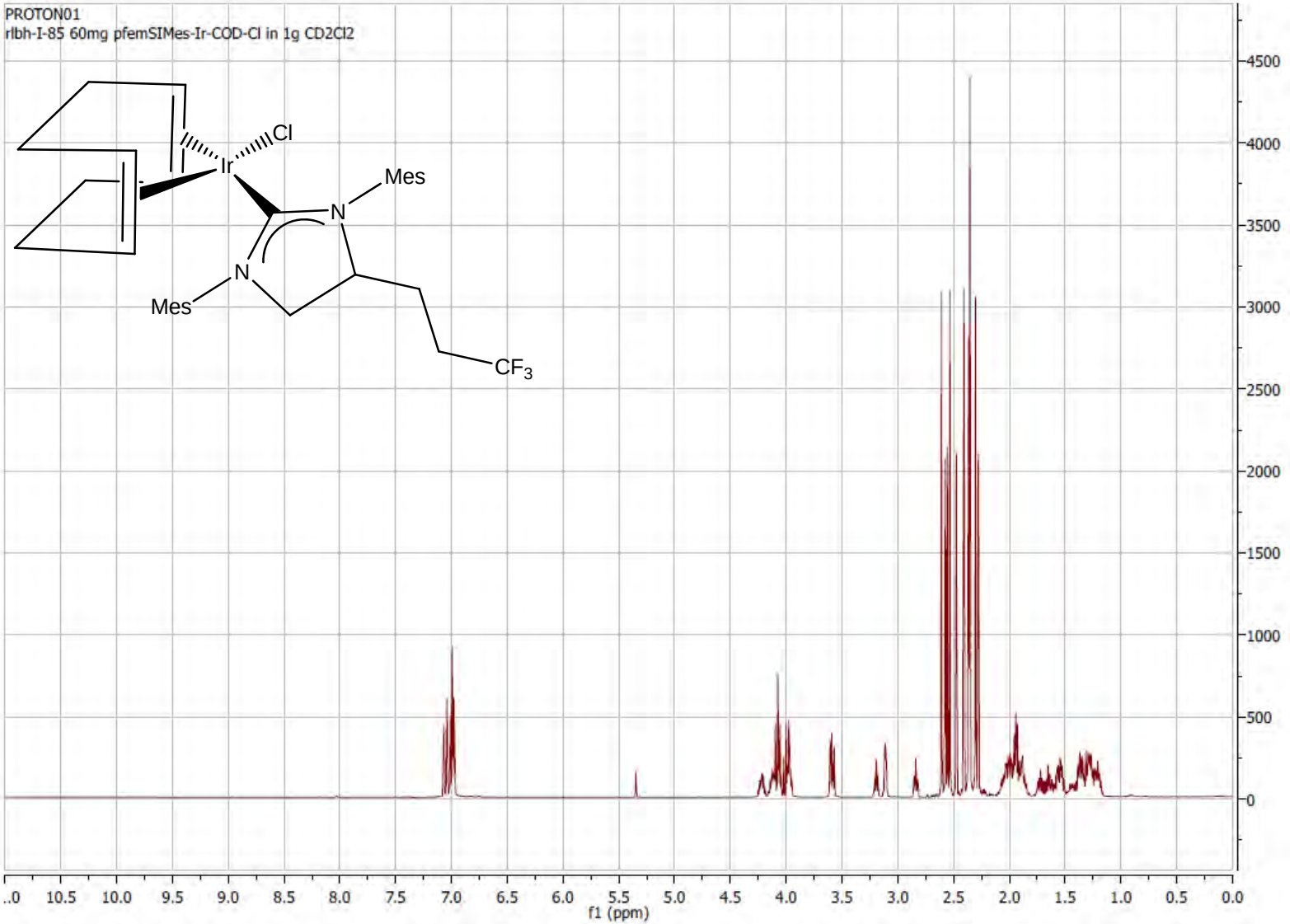


- **Very general reaction pathway: suitable for all Grignard reagents**
- **Attempts at dialkylation unsuccessful**
- **Slight excess of Grignard reagent ensures complete monoalkylation**

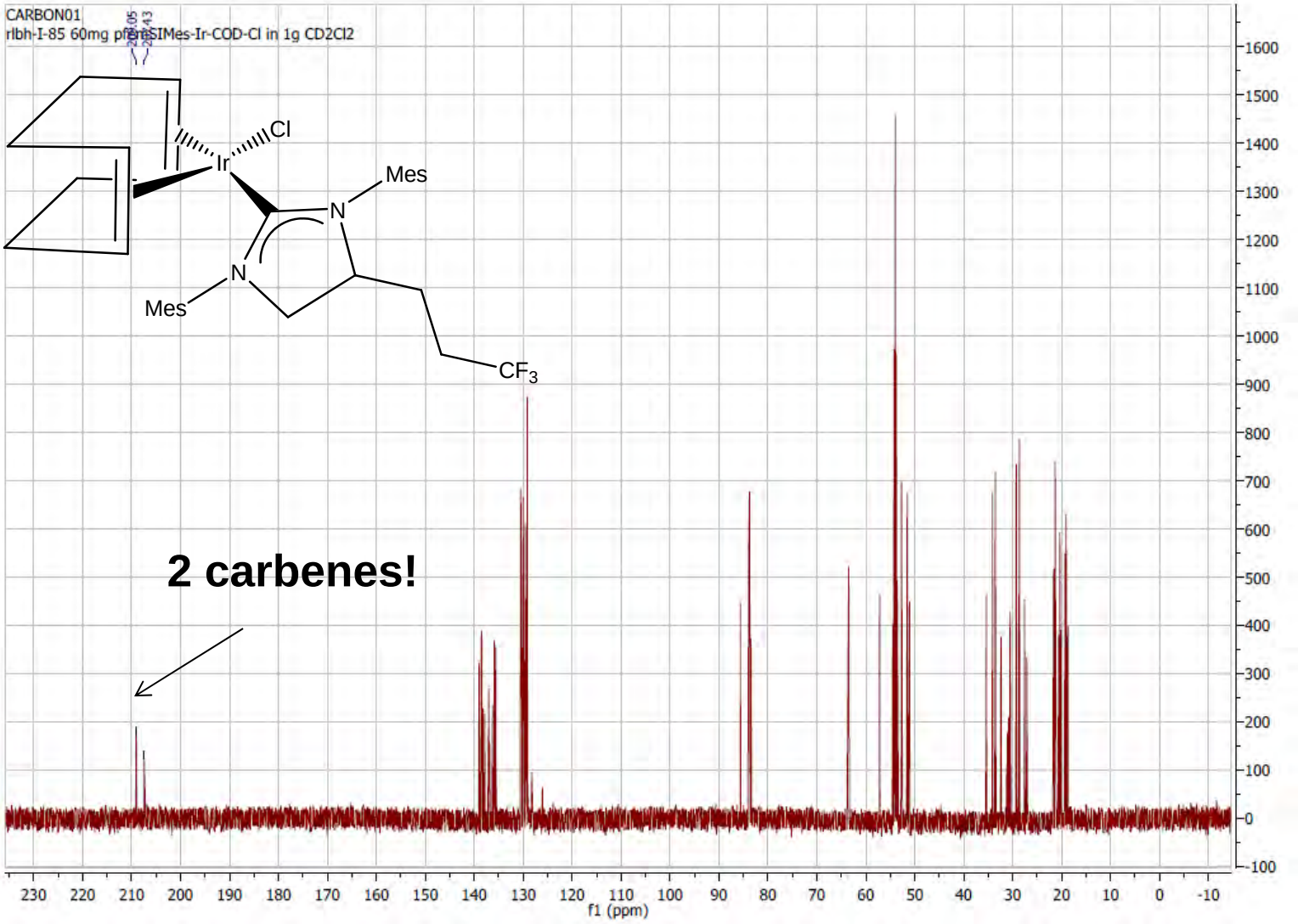
^{1}H Spectrum of pfme-SIMes+Cl-



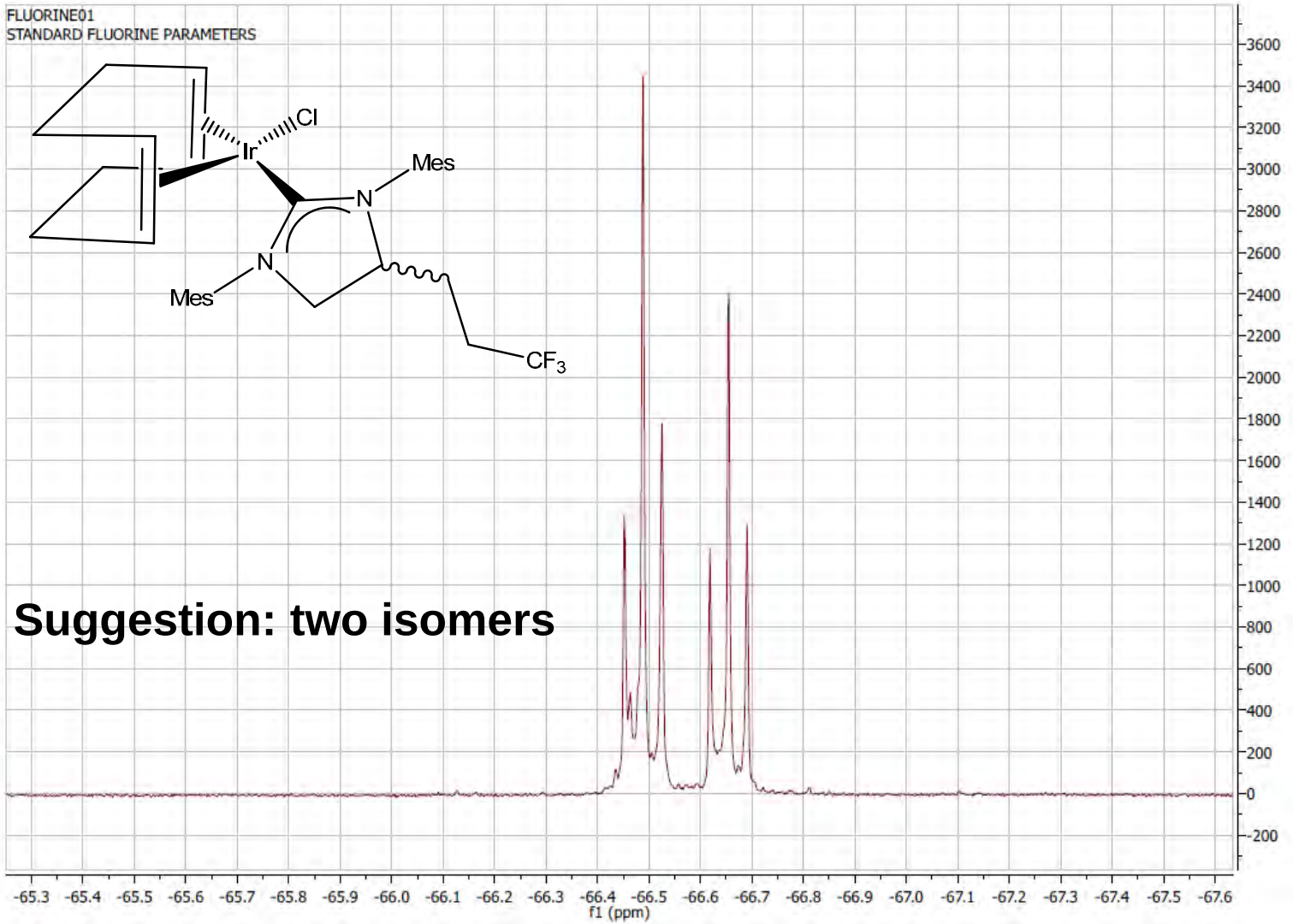
^{1}H Spectrum of pfme-SIMes-IrCOD-Cl



^{13}C Spectrum of pfme-SIMes-IrCOD-Cl

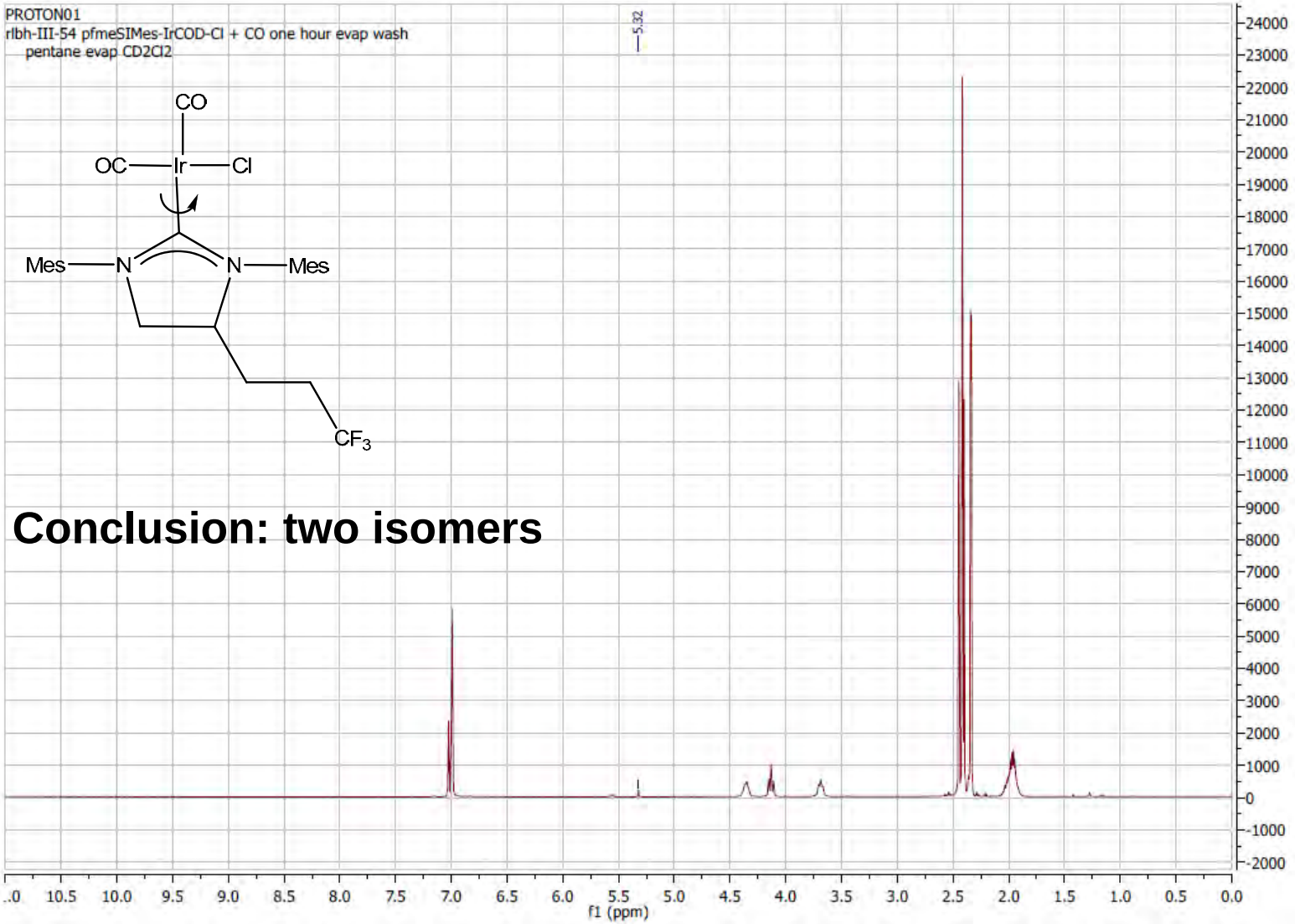


^{19}F Spectrum of pfme-SIMes-IrCOD-Cl



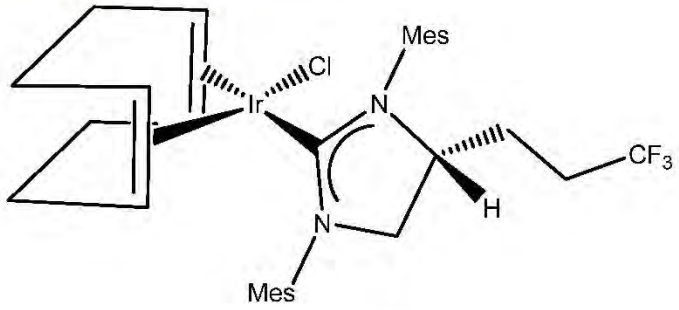
Suggestion: two isomers

^{1}H Spectrum of pfme-SIMes-Ir(CO)$_2$-Cl

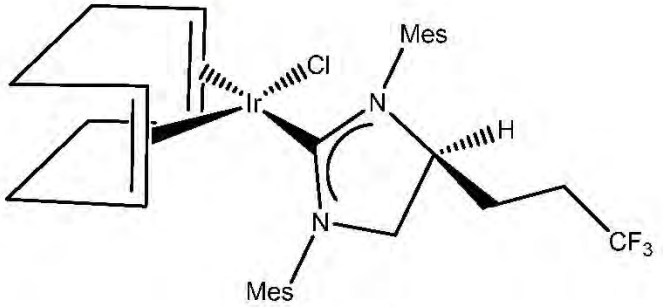


Conclusion: two isomers

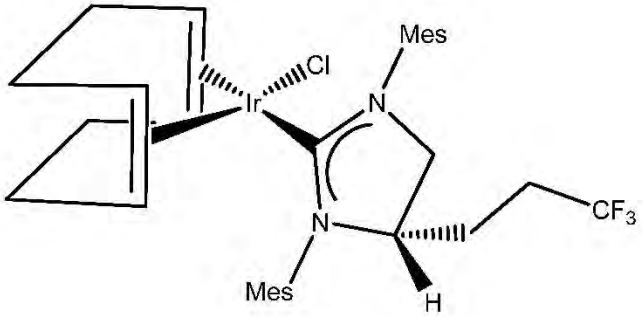
Potential Isomers in Solution



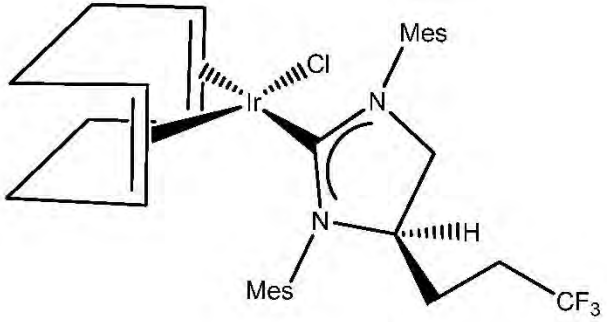
Isomer A



Isomer B



Isomer C



Isomer D

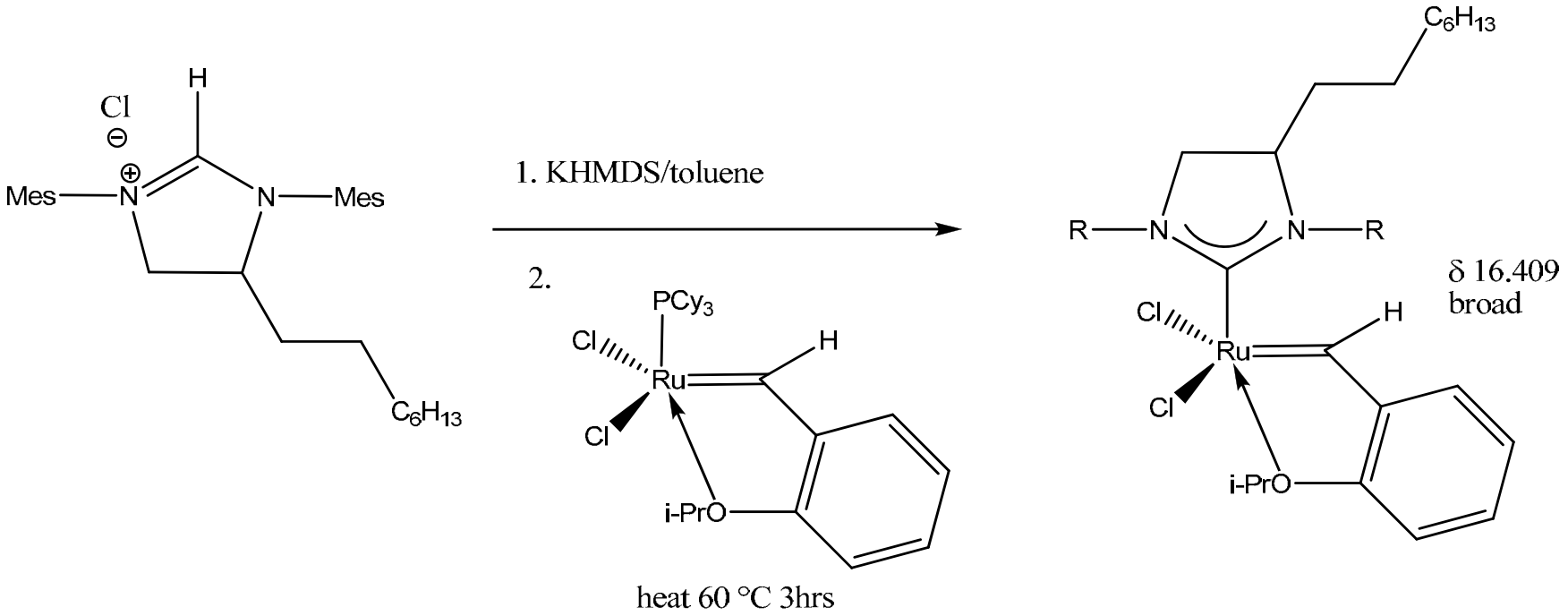
- **Ligand rotation observed upon heating in toluene-d_8**

Backfluorinated NHC Complexes with $(CO)_2$-Ir-Cl in CD_2Cl_2(cm^{-1})

Compound	Functional Group	νCO 1st CO	νCO 2nd CO	νCO Avg.
SIMes	H	2068.0	1981.2	2024.6
pfme-SIMes	$CF_3CH_2CH_2$	2068.8	1981.9	2025.4
pfbe-SIMes	$F(CF_2)_4CH_2CH_2$	2068.8	1981.9	2025.4
pfhe-SIMes	$F(CF_2)_6CH_2CH_2$	2069.1	1982.0	2025.6
pfoe-SIMes	$F(CF_2)_8CH_2CH_2$	2069.1	1982.0	2025.6
pfde-SIMes	$F(CF_2)_{10}CH_2CH_2$	2069.1	1982.1	2025.6
pfop-SIMes	$F(CF_2)_8CH_2CH_2CH_2$	2068.5	1981.2	2024.8

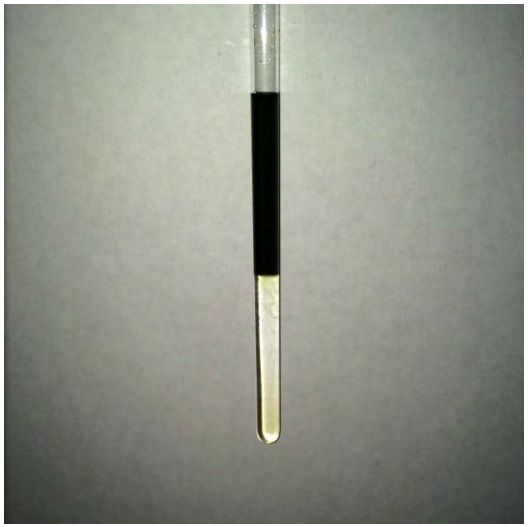
When buffer length is CH_2-CH_2, the perfluoroalkyl group appears to have a small electronic effect

Synthesis of Ru Complexes



- **Green solid (same color as 2nd generation catalyst)**
- **Complex demonstrates metathesis activity**
- **Perfluorodecylethyl, perfluorooctylethyl and perfluorooctylpropyl complexes also synthesized**

Partition Study



- **Partition study with pfheSIMes 2nd Generation Grubbs-Hoveyda catalyst with toluene (upper phase) and perfluoromethyl cyclohexane (lower phase)**
  - **Insufficient backfluorination to improve solubility in perfluoromethylcyclohexane**

Backfluorinated NHC Carbene complexes

- **Conclusions**
  - **A series of backfluorinated imidazolinium NHC carbene complexes were synthesized**
  - **Each backfluorinated NHC carbene-COD-iridium chloride complex is a mixture of two observable isomers due to the lack of rotation of the NHC carbene ligand**
  - **The backfluorinated NHC carbene-dicarbonyl-iridium chloride complex is single compound due to rotation of the NHC carbene ligand**
  - **An IR study of the backfluorinated NHC carbene-dicarbonyl-iridium chloride complexes determined that the addition of a perfluoroalkyl chain slightly changes the electronics of the molecule.**

Backfluorinated NHC Carbene complexes

- **Conclusions – Cont'd**
  - **The IR study of the backfluorinated NHC carbene-dicarbonyl-iridium chloride complexes also suggest that the electronic effects of the perfluoroalkyl group is independent of perfluoroalkyl chain length**
  - **A series of the longer chain backfluorinated NHC Ruthenium alkylidene complexes were synthesized**
  - **These complexes demonstrated metathesis activity similar to the nonflourinated alkylidene complex**

Backfluorinated NHC Carbene Complexes

- **Future Work**
  - **Look for methods to increase the amount of backfluorination of imidazolinium complexes**
  - **Investigate the electronic effects of side fluorination of aromatic rings of imidazolinium complexes**
  - **Investigate the use of the technology for other applications in order to improve sustainability**

Acknowledgements

- **Air Force**
- **Leslie Peasant (AFOSR)**
- **Dr. Ken Caster (AOARD)**
- **Kristen Schario (CRADA)**
- **Dr. Chastity Whitaker (CRADA)**
- **Lt. Col Brian Tidball (RQRC)**
- **Dr. Stephen Rodgers (RQR)**
- **Dr. Taewoo Park (RQR)**
- **Dr. Shawn Phillips (RQR)**
- **Dr. Siva Banda (RQ)**
- **Cal Tech**
- **Prof Grubbs**
- **Linda Syme (Admin)**
- **Grubbs Group**
- **Farnaz Bakhshi (CRADA)**
- **Dr. Dave Vandervelde (NMR)**